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Comparison of Audit Techniques and Performance Audit Results for EPA Method 25 for Volatile Organic Compounds

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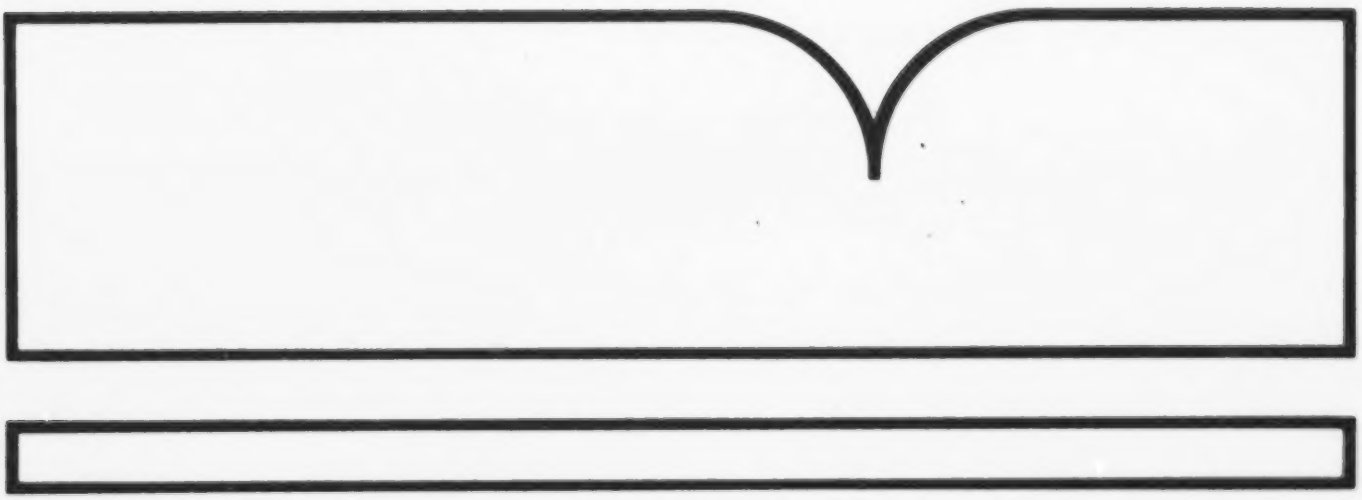

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COMPARISON OF AUDIT TECHNIQUES AND PERFORMANCE AUDIT RESULTS FOR EPA METHOD 25 FOR VOLATILE ORGANIC COMPOUNDS

by

R. K. M. Jayanty and G. B. Howe
Research Triangle Institute
Research Triangle Park, NC 27709

D. J. von Lehmden, R. G. Fuerst, T. J. Logan, and M. R. Midgett
Environmental Monitoring Systems Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

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D. J. von Lehmden

ENVIRONMENTAL MONITORING SYSTEMS LABORATORY
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U.S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NC 27711

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16. ABSTRACT Organic audit materials have been developed by U.S.Environmental Protection Agency to evaluate quality of measurements made by federal, state and local agencies or their contractors during compliance source tests. Among audit materials are materials for auditing EPA Method 25, a method for measuring source emissions of volatile organic compounds. Two types of audit materials for Method 25 have been developed and validated by inter- and intra-laboratory studies. The first type makes use of commercially available gas cylinders containing known concentrations of selected volatile organics in an inert balance gas. The second type involves use of a stainless steel cartridge containing a solid sorbent (Tenax®) spiked with known quantities of selected organic compounds to generate organic vapors quantitatively using thermal desorption. Organic vapors generated are collected and analyzed using Method 25 procedures as published in the Federal Register. Results of inter-laboratory studies conducted on two separate occasions, with both audit techniques, show close agreement with Research Triangle Institute measured concentrations for high concentration mixtures; however, a wide range was obtained for low concentration mixtures. Studies were also performed to determine the stability and feasibility of using the materials in performance audits. Results indicate both types of audit materials are stable and useful in conducting EPA Method 25 audits. Performance audit results using gas cylinders for EPA Method 25 during compliance source tests are included. These audit results generally were within ± 25% of the audit concentration.

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COMPARISON OF AUDIT TECHNIQUES AND PERFORMANCE AUDIT RESULTS FOR EPA METHOD 25 FOR VOLATILE ORGANIC COMPOUNDS

R. K. M. Jayanty, and G. B. Howe
Research Triangle Institute
Research Triangle Park, North Carolina 27709

D. J. von Lehmden, R. G. Fuerst, T. J. Logan, and M. R. Midgett
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

Organic audit materials have been developed by U. S. Environmental Protection Agency to evaluate the quality of measurements made by Federal, State, and local agencies or their contractors during compliance source tests. Among the audit materials are materials for auditing EPA Method 25. EPA Method 25 is a method for measuring source emissions of volatile organic compounds. This method has been used extensively. Two types of audit materials for EPA Method 25 have been developed and validated by interlaboratory and intralaboratory studies. The first type makes use of commercially available gas cylinders containing known concentrations of selected volatile organics in an inert balance gas. The second type involves the use of a stainless steel cartridge containing a solid sorbent (Tenax®) spiked with known quantities of selected organic compounds to generate organic vapors quantitatively using thermal desorption. The organic vapors generated are collected and analyzed using EPA Method 25 procedures as published in the Federal Register.[1] Results of interlaboratory studies conducted on two separate occasions, with both of the audit techniques, show close agreement with Research Triangle Institute measured concentrations for high-concentration mixtures, however, a wide range was obtained for low-concentration mixtures. Similar results were obtained by other researchers using Method 25 procedures. Studies were also performed to determine the stability and feasibility of using the materials in performance audits. Results indicate that both types of audit materials are stable and useful in conducting EPA Method 25 audits. Performance audit results using gas cylinders for EPA Method 25 during compliance source tests are included. These audit results generally were within ± 25 percent of the audit concentration.

Introduction

The U.S. Environmental Protection Agency (EPA) is interested in developing audit materials for all EPA Source Reference Methods. These audit materials are used to conduct performance audits during stationary source measurements. The performance audit involves providing "unknown" or "blind" samples to the source testing organization for analysis. When conducted simultaneously with a source emission test, the performance audit provides an assessment of measurement accuracy. Accuracy determinations are used in setting standards and assessing compliance test results after emission standards have been promulgated.

The Quality Assurance Division of EPA's Environmental Monitoring Systems Laboratory has a program to assess the accuracy of source emission measurements. The program is operated for EPA by the Research Triangle Institute (RTI). The program consists of performance audits of source emission measurement systems using a variety of developed audit materials. The most requested audit materials are for performance audits of EPA Method 25. This method is for measuring source emissions of volatile organic compounds. RTI has developed and validated two types of audit materials for auditing both the sampling and analytical phases of EPA Method 25. The first material makes use of commercially available gas cylinders containing known concentrations of selected volatile organics in an inert balance gas. The second material involves the use of a stainless steel cartridge containing a solid sorbent (Tenax®) spiked with known quantities of selected organic compounds to generate organic vapors quantitatively using thermal desorption. During the development the organics generated were collected and analyzed in RTI's laboratory using EPA Method 25 procedures as published in the Federal Register.[1] These two audit methods were also evaluated at two concentration levels by different laboratories on two separate occasions to determine repeatability, reproducibility, and accuracy. The design, testing and comparison of the two audit techniques and examples of performance audit results are described in this paper.

Experimental Procedures

Audit Material Development and Verification

Gas Cylinders -- Gas cylinders containing known concentrations of organic compounds and a 5 percent carbon dioxide/95 percent nitrogen balance gas were purchased from a commercial manufacturer. The purpose of the CO_2 is twofold: (1) to test the analysis capability of purging CO_2 contained in the EPA Method 25 condensate trap before recovery of condensed organics, and (2) to test the capability of the nonmethane organic analyzer in separation and quantifying low-concentration organics in the presence of high-concentration CO_2. The cylinders contents were analyzed periodically by gas chromatography with flame ionization detector to corroborate the concentrations reported by the manufacturer, to provide analysis data to check the stability, and for the interlaboratory analysis program.

Spiked Cartridges -- U-shaped type 316 stainless steel cartridge (dimensions: 35.56 cm or 45.72 cm length x 0.95 cm diameter x 0.12 cm wall thickness) containing 2 to 3 gm of Tenax® were spiked with known quantities of selected organic compounds and thermally desorbed at temperatures from 160 to 180 °C to generate organic vapors quantitatively. After packing, the ends of the cartridges are plugged with glass wool. The cartridges are conditioned for 3 h by purging with nitrogen and heating to 180 °C. Then, a known quantity of an organic mixture is injected directly into the inlet side of the Tenax® bed using a long-needle syringe. The cartridge is capped immediately after the injection.

Since room air contains CO_2 and may contain unwanted organic contaminants, CO_2-and hydrocarbon-free air (grade 0.1) from a compressed gas cylinder were delivered through a glass manifold to the inlet of the cartridge at atmospheric pressure. The organic sample was then drawn from the heated (160 to 180 °C) Tenax® cartridge using EPA Method 25 collection procedures (see Figure 1). Briefly, the desorbed organic sample was collected into a chilled condensate trap and an evacuated 6-L sample tank. The total gaseous nonmethane organics (NMO) were then determined by combining all results obtained from separate analyses of the condensate trap and sample tank fractions. The organic contents of the condensate trap were oxidized and quantitatively collected in an evacuated vessel, and an aliquot of the resulting CO_2 was reduced to methane and measured by a flame ionization detector (FID). An aliquot of the gas collected in the sample tank was introduced into a gas chromatographic system to separate the nonmethane organics from carbon monoxide (CO), carbon dioxide (CO_2), and methane (CH_4). After this separation, the NMO were oxidized to CO_2, reduced to methane, and measured by an FID.

Interlaboratory Test Plan

Four laboratories having past experience in source testing using EPA Method 25 procedures were selected for an interlaboratory study. Two cylinders representing two concentration levels (low and high) were shipped to four laboratories for analyses to evaluate the feasibility of using these as audit material for EPA Method 25. Seven spiked cartridges (six test and one practice) representing two concentration levels were shipped on two separate occasions to each of the four laboratories for analyses to evaluate the feasibility of using these as audit material for EPA Method 25. In each set of seven cartridges, there were three low-concentration samples (1-μL injection) and three high-concentration samples (5-μL injection) plus one practice cartridge at either low (1 or 2-μL injection) or high (5-μL injection) concentration. The practice cartridge was provided to each laboratory to become familiar with the audit technique. General instructions to perform the experiments and data sheets for reporting the results were also sent to each laboratory. The laboratories were informed that these audit materials were not for an actual audit but only for an evaluation of the audit material and that the types of organics were not disclosed. The interlaboratory testing of the two audit materials were performed at different times and the participating laboratories may not be the same.

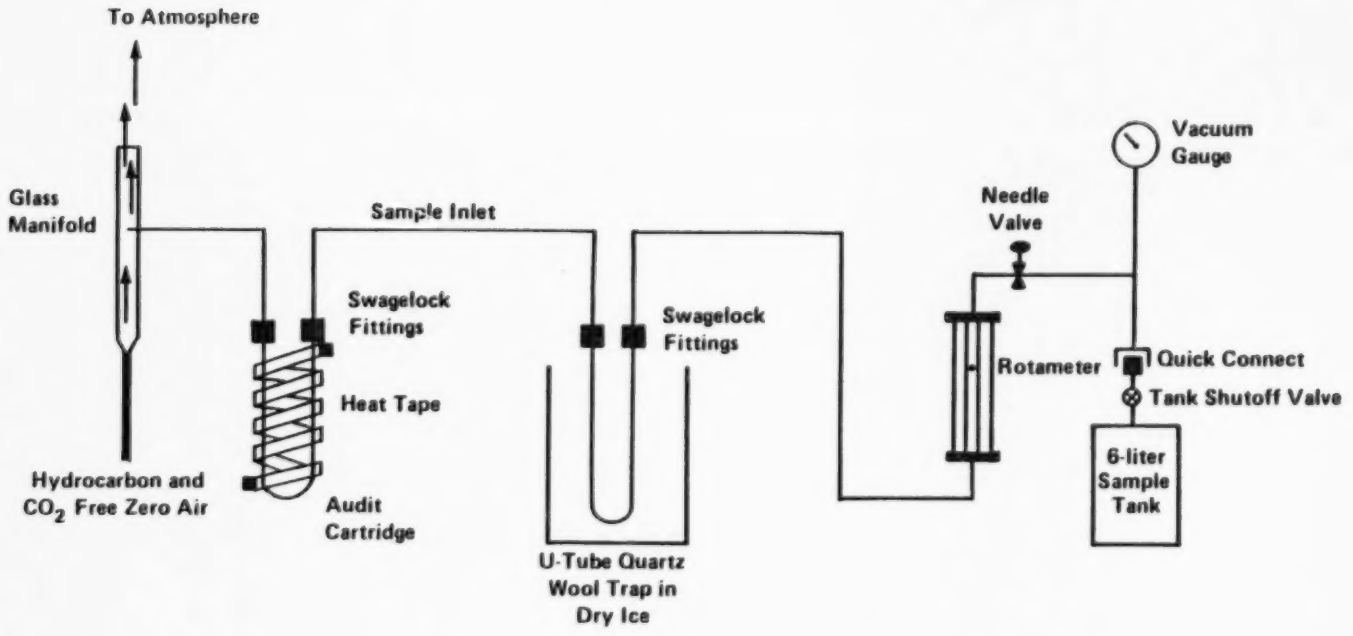

Figure 1. Audit cartridge with Method 25 sampling train.

Results and Discussion

Interlaboratory Test Results

Gas Cylinders -- The results of the analyses of the two audit gas cylinder samples by the different laboratories and percent bias compared with the RTI concentrations are shown in Tables 1 and 2. In Table 1, all of the laboratories except one reported concentrations within approximately 5 percent of the RTI value for analysis of the high-concentration mixture. Results of analyses of the low-concentration mixture ranged from 15 to 124 percent different from the RTI value. Possible problems indicated by the low-concentration cylinders analysis results are trap contamination, insufficient purge of carbon dioxide from the condensate trap prior to organic recovery, and NMO analyzer deficiency.

Spiked Cartridges -- The results of the analyses of the spiked cartridges by the different laboratories on two separate occasions using EPA Method 25 procedures are shown in Table 3. (Results of the practice cartridges provided are not presented in this table.) The expected total organic concentrations of the spiked cartridges were based on theoretical concentrations calculated from the amount of organic mixture injected onto the Tenax®. The reported results show close agreement with the expected values. For example, results of analyses of the low-concentration cartridges ranged from -22.8 to +20.7 percent different from the expected values. Likewise, the results of analyses of the high-concentration cartridges ranged from -14.5 to +6.2 percent different from the expected values. Statistical analysis of the results are published elsewhere.[2]

Stability Studies

Data collected over time on the audit materials are used to estimate the stabilities of these audit materials. Stability data are important for several reasons. First, the organic compounds must be stable to be considered by EPA as a reliable audit material. Second, if organics are stable, other investigators may decide to use these types of materials as calibration standards and/or quality control check samples. Finally, if organics are stable in the audit material, future EPA regulations may include performance audits as a means of assessing the accuracy of the measurement systems.

The term "stability", as it pertains to organic compounds, is defined here as the absence of change in concentrations over time at a specified concentration level. The audit materials are analyzed as soon as they are prepared and later analyzed at periodic intervals. Examples of stability data for both types of audit methods are shown in Tables 4 and 5. These results demonstrate that both types of audit materials are stable within experimental error over a long period. The stability study is an on-going process.

Table 1

Interlaboratory Results: High-Concentration Gas Mixture Analysis[a]

Laboratory	Reported results (ppm C)			Percent bias[b]
	Noncondensible fraction	Condensible fraction	Total	
RTI	1,238	706	1,944	--
A	1,445	490	1,935	-0.5
B	859	978	1,837	-5.5
C	1,002	944	1,946	+1.0
D	1,066	537	1,603	-17.5

[a] Manufacturer concentration = 1,960 ppm C.

[b] $\% \text{ bias} = 100 \times \frac{\text{lab-reported total conc.} - \text{RTI-measured total conc.}}{\text{RTI-measured total concentration}}$

Table 2

Interlaboratory Results: Low-Concentration Gas Mixture Analysis[a]

Laboratory	Reported results (ppm C)			Percent bias[b]
	Noncondensible fraction	Condensible fraction	Total	
RTI	55	42	97	--
B	48	169	217	+123.7
D	105	47	152	+56.7
E	63	49	112	+15.5

[a] Manufacturer concentration = 101 ppm C.

[b] $\% \text{ bias} = 100 \times \frac{\text{lab-reported total conc.} - \text{RTI-measured total conc.}}{\text{RTI-measured total concentration}}$

Table 3

Interlaboratory Results: Spiked Cartridge Analysis

Lab No.	Expected total concentration, ppm C[a]	Reported total concentrations, ppm C[a]											
		Low						High					
		1	2	3	4	5	6	1	2	3	4	5	6
1	204	b	182	187	213	212	211						
	1,019							b	890	879	1036	960	950
2	204	183	243	204	194	232	222						
	1,019							872	b	899	b	977	918
3	204	228	191	218	176	157	179						
	1,019							1082	890	967	883	831	1007
4	204	207	246	201	b	b	b						
	1,019							983	1063	945	b	b	b

[a] Based on an assumed 6-L sample volume.
[b] Values either discarded or not reported because of analytical problems.

Table 4
EPA Method 25 Cylinder Gas Mixture Stability Study[a]

Number of Days/Concentration	A	B	C
1st RTI Analysis Date	3/16/83	3/16/83	12/11/84
ppm C	(775)	(1,040)	(98.9)
Day[b]	483	483	90
ppm C	(779)	(1,060)	(93.3)
Day[b]	726	726	443
ppm C	(765)	(1,020)	(99.6)
Day[b]	1079	1079	
ppm C	(806)	(1,093)	

[a] Gas mixture contains an aliphatic hydrocarbon, an aromatic hydrocarbon, and a carbon dioxide in nitrogen.
[b] Number of days after 1st RTI analysis date.

Table 5
Spiked Cartridges Stability Study Results

Number of days	Expected total concentration, ppm C[a]	Measured Total Concentration, ppm C[a]	Percent difference[b]
0	204	202	1.0
7	204	206	1.0
17	204	202	-1.0
24	204	207	1.5
31	204	203	-0.5
36	204	209	2.5
60	204	207	1.5

[a] Based on an assumed 6-L sample volume.

[b] $\% \text{ difference} = 100 \times \frac{\text{measured total conc.} - \text{expected total conc.}}{\text{expected total concentration}}$

Performance Audits

As stated previously, the EPA (through RTI) provides audit materials for performance audits upon request from the Federal, State, or local agencies or their contractors. The contractors must, however, be performing source emission tests on behalf of EPA or one of these other agencies to qualify for the performance audit. It is recommended the performance audit be conducted simultaneously with the actual planned source test. Performance audits conducted prior to source tests to assess the proficiency of the measurement system (including the sampling and analytical personnel) are also encouraged.

To date, 20 audits have been conducted with EPA Method 25 gas cylinders. Performance audits with spiked cartridges have not yet been initiated. The results for completed performance audits are shown in Table 6. Agreement of $\pm$ 25 percent with the audit concentrations measured by RTI is acceptable on EPA Method 25 audits.

The principal results of these audits have been to ensure that analyses are performed properly, to detect problems that could be corrected, and to document the accuracy of the measurement systems used during the source compliance tests.

Conclusions and Recommendations

Two types of audit materials containing volatile organics at ppm levels have been developed for auditing/evaluating both the sampling and analytical phases of EPA Method 25 in the field. The interlaboratory results obtained showed good agreement (particularly at higher levels) between reported and expected concentrations based on either RTI measurements or the theoretical loadings. Both types of audit materials were stable over a long period. It is recommended that a performance audit using either the compressed cylinder gas mixtures of organics or spiked cartridges be used during future EPA Method 25 source emission tests as a routine quality assurance procedure. Federal, State, and local agencies and their contractors may request a performance audit by contacting Mr. Robert L. Lampe, EPA, Environmental Monitoring Systems Laboratory, Quality Assurance Division, Research Triangle Park, North Carolina, 27711.

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Table 6

EPA Method 25 Performance Audit Results During Compliance Source Tests Using Gas Cylinders

Audit No.	Industry/source tested	RTI-measured conc. (ppm C)	Client audit result bias (percent)[a]
128	Surface coating	205	+21.5
		1,040	+18.9
135	Polyester resins production	104	+28.1
149	Plastic manufacturing	764	- 9.3
150	Wire coating	1,020	-48.2
156	Wire coating	187	+52.0
169	Solvent ink coating operation	196	+30.6
		1,093	+13.4
172	Solvent coating	196	+25.0
		806	+ 3.0
161	Printing operation	1,930	+16.0
		187	+55.0

[a]Client percent bias = $100 \times \frac{\text{Client measured conc. - RTI-measured conc.}}{\text{RTI measured conc.}}$

References

1. Method 25, - "Determination of total gaseous nonmethane organic emissions as carbon," Federal Register 45 (194): October 1980.

2. R. K. M. Jayanty, J. A. Sokash, G. B. Howe, et al., "A new audit technique for EPA Method 25," J. of Air Pollution Control Assoc. 36 (12): December 1986.